

NANOCOMPOSITE FIBERS BASED ON PHASE SEPARATING POLYMER BLENDS

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ABSTRACT

We have investigated phase separating immiscible polymer blends of a polymer melt and a polymer solution as a means to produce composites with features on a submicron length scale. A 2D cell dynamics code for modeling phase separation in a flow field has been modified to include features such as a boundary which favors one component and a flow profile for a power law fluid. The simulations indicate that the skin formation seen experimentally is driven by surface energy effects rather than viscosity. In pressure driven flow a power law fluid is predicted to have a more pronounced sheath core structure than a Newtonian fluid.

1. INTRODUCTION

The spinning of fibers from blends of phase separating polymer melts and polymer solutions is largely unexplored. In general, polymers are not mutually soluble because of the entropic contribution to the free energy of mixing. Therefore most polymer blends will phase segregate over time, a phenomenon that has been widely studied. An area that has received very little attention is phase separation between polymer melts and polymers in solution. Many polymers of current interest are not melt processable, including conducting polymers, biopolymers such as DNA and proteins, biodegradable polymers, and very high strength polymers such as Kevlar®.

Combining melt and solution spun polymers into a single fiber opens up the possibility of previously unattainable combinations of materials and properties combined with the ease of melt processing. The development of internal structure during the spinning process provides opportunities for additional complexity. Furthermore, the solution phase can provide a means of carrying out chemical reactions such as using sol-gel chemistry to synthesize ceramic particles within the fiber. Utilizing this approach, it may be possible to create self assembling device fibers, such as photovoltaic, battery and sensor fibers.

The large number of variables and the complexity of the phase space have led us to undertake a fundamental study of the behavior of these blends combining fiber spinning of blends of polycaprolactone (PCL) and polyethylene oxide (PEO) and computational modeling. The initial experimental results have been previously reported (Drew 2007). For modeling we have utilized a cell-dynamics phase segregation model developed by the Balazs Research group at the University of Pittsburgh to predict phase morphology development during flow. The code has been slightly modified to investigate different velocity profiles and the effects of surface characteristics.

1.1 Applications of the Blends of Polymer Melts and Polymer Solutions.

Polymer blends have received considerable attention because of the potential to make relatively inexpensive composite materials. While polymer blends have been widely studied, one area that has received little attention is the blending of polymer solutions and polymer melts. By combining a polymer melt and a polymer solution we hope to accomplish several objectives. First, we aim to maintain the simplicity and efficiency associated with melt processing, yet extend this method to include polymers that are not melt processable. For example many conducting polymers have stiff backbones due to extended conjugation and require solution processing. A second objective is to broaden the selection of polymers by having access to both melt processed and solution processed polymers. For instance, processing of piezoelectric and magnetoelectric materials within the composite could lead to advances in power harvesting and sensor technology (Priya 2007). Finally, the presence of a solution phase allows us to take advantage of chemistries that involve reactions and/ or sol-gel processing.

With this in mind we have investigated the extrusion of a blend of melt processable polycaprolactone (PCL) and a solution of polyethylene oxide (PEO) in water. Polyethylene oxide has many practical uses, including biological and electronic applications, which may be

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exploited by this method. PEO has been shown to be an effective vehicle for controlled drug delivery (Park 1994) where the timing and dosage of the drug release may be manipulated by the polymer blend structure. PEO can be utilized for live cell encapsulation within a polymer blend scaffold to facilitate tissue regeneration (Sims 1996). Polyethylene oxide may also be used in solid polymer electrolytes. Solid electrolytes consist of ionic species (e.g. lithium salts) and PEO. By chelating the ions, the PEO hinders ionic recombination yielding higher conductivities than the conductivity of the ionic materials alone (Fan 1997).

We have modeled the process using a cell dynamics approach with a loosely coupled flow field, where the flow field is simply imposed on the phase separating blend. The velocity profile is either that of a Newtonian fluid or power law fluid in fully developed flow through a cylindrical pipe. Non-Newtonian effects are probably limited in the experimental process we used because the shear rate is low. However, in a commercial process one would like to run at high speeds and hence shear rates.

1.2 Extrusion of PCL/PEO Blends.

The experimental part of the work was conducted using a laboratory scale twin screw extruder to produce micron size fibers, rods and spheres embedded in the fiber matrix as well as a co-continuous morphology. The two polymers are blended by recirculating the mixture through the co-rotating twin screw extruder, and then the mixture is extruded through a cylindrical exit die where the mixture phase separates through spinodal decomposition. In most cases the melt spun PCL forms a sheath due to its lower surface energy, with the micron size features embedded in the core of the fiber. The morphology of the spun fibers was examined by scanning electron microscopy after dissolving away the PEO phase. We will review this previously published work, and present the results of the modeling. We will also discuss the potential for more complicated structures utilizing phase segregation and multicomponent fiber spinning.

2. THE CELL DYNAMICS MODEL

The base model was developed by researchers at the University of Pittsburgh, which is based on a cell dynamical system model (Oono 1988). This code was generously provided to us for this work. Only a very brief outline of the base model is provided here. An imposed pressure gradient drives the flow of two immiscible fluids, A and B. To characterize the morphology of the fluid we define an order parameter, which is simply the difference between the concentrations of phase A and phase B at each node. The

average order parameter is specified initially and then a random variable is added to each node to produce a distribution around the average value. In this model, the order parameter is conserved.

The change in the order parameter (i.e. local density of A and B) with time is given by the Cahn-Hilliard Equation:

$$\frac{\delta\phi}{\delta t} + \vec{u} \cdot \vec{\nabla} \phi = M \nabla^2 \mu \quad (1)$$

where:

ϕ = order parameter

t = time

u = velocity profile

M = mobility of the order parameter

μ = chemical potential

The chemical potential is the change in free energy with the order parameter $\mu = \delta F / \delta \phi$ where F is the Ginzburg-Landau free energy.

The order parameter is known at all locations and the velocity profile is specified and “loosely coupled” meaning the velocity profile is unchanged by the variation in the density of the two components. The mobility, M , of the order parameter is a scalar specified at the start of the simulation. Only the chemical potential needs to be calculated. The chemical potential at each node is then calculated by minimizing the Ginzburg-Landau free energy of each node and its four nearest neighbors and next nearest neighbors (diagonals). The model space is a square lattice with 400x400 sites. We use a cell dynamic system method to update the value of ϕ (Oono 1988).

2.1 Non-neutral Surfaces.

In order to simulate surfaces with a surface energy favoring one of the components, a value of the order parameter was assigned to the surface nodes. In effect, the surface is defined to be composed of a fixed amount of A and B, typically less than 100% A or B. The calculations are then carried out as usual. Following the Ginzburg-Landau free energy minimization an amount of A will have moved either to or from the surface. In order to keep the surfaces from being either a source or sink of A or B the amount of the order parameter transferred from the surface in the free energy minimization is then subtracted from the first layer of the polymer.

2.2 Power Law Fluid Flow

Most polymer melts and solutions are shear thinning i.e. as the shear rate increases the apparent viscosity decreases. Equation 2 shows the relationship between the shear stress (τ) and shear rate ($d\nu/dx$), where K and n are characteristics of the fluid. The special case when $n=1$ corresponds to a Newtonian fluid and then K is just the usual viscosity. For a shear thinning power law fluid $n < 1$, and values of n typically lie between 1/3 and 1/2. The shear rate increases with increasing flow rate and decreasing pipe dimension. There are many practical considerations that result from the power law nature of polymers (e.g. extruder power consumption and volumetric flow rate as a function of pressure drop). We are mostly concerned here with the effects on morphology.

$$\tau = K \left(\frac{d\nu}{dx} \right)^n \quad (2)$$

The velocity profile of a power law fluid in pressure driven flow through a pipe of circular cross section is given by equation 3 (Middleman, 1977).

$$v_x = \frac{nR}{1+n} \left(\frac{RH}{2K} \right)^{1/n} \left[1 - \left(\frac{r}{R} \right)^{1+1/n} \right] \quad (3)$$

Qualitatively, for a power law fluid the flow profile approaches "plug flow" where there is a sharp velocity profile at the edge and a relatively constant velocity across the center of the pipe, in contrast to the parabolic velocity profile of a Newtonian fluid. For a power law fluid the shear is concentrated at the edge while the center experiences relatively little shear.

In order to adapt equation 3 to a square lattice where the lattice points extend from one side of the pipe to the other rather than from the center line out radially, we define a new variable $r^* = (r+R)/2R$. In terms of the j th node (from $j=0$ to $j=L_y$ perpendicular to the flow), $r^* = (j-1)/(L_y-1)$. From there it is a straight forward matter to write an equation to express the flow profile in terms of the pressure drop per unit length, H , and the constants of the power law equation, most notably the power law exponent, n .

$$V[j] = \frac{n}{1+n} \left(\frac{H}{2K} \right)^{1/n} \left(\frac{L_y-1}{2} \right)^{1+1/n} \left\{ 1 - \left[2 \left(\frac{j-1}{L_y-1} - 1 \right) \right]^{1+1/n} \right\} \quad (4)$$

The velocity V is zero at $j = 1$ and $j = L_y$ (the "no slip" boundary condition) and the walls are at $j = 0$ and $j = L_y+1$.

To facilitate comparison with a Newtonian fluid we normalized the velocity profile using the volumetric flow rates. The volumetric flow rate for a power law fluid is given by

$$Q_{PL} = \frac{n\pi R^3}{1+3n} \left(\frac{RH}{2K} \right)^{1/n} \quad (5)$$

For a Newtonian fluid $n = 1$, and we can divide the volumetric flow rate for the Power Law case, Q_{PL} , by the volumetric flow rate for a Newtonian fluid, Q_N , and get

$$Q_{PL}/Q_N = \frac{4n}{1+3n} \left(\frac{RH}{2K} \right)^{\frac{1}{n}-1} \quad (6)$$

Dividing the equation for the velocity profile by Q_{PL}/Q_N eliminates the power law exponent, n , from H , so that, like a Newtonian fluid, $V[j]$ is linearly proportional to the pressure gradient H .

3. SIMULATION RESULTS

3.1 Effects of Surface Energy

A blend of PCL and PEO at 1:1 ratio was extruded and is shown in Figure 1a. The PEO phase has been dissolved away. The uniform co-continuous core of the fiber is undisturbed and there is a skin of PCL with a sharp transition from the skin to the co-continuous morphology. Generally, the less viscous phase in a molten blend will migrate to the extruder die wall where the shear rate is highest, whereby minimizing energy and pressure drop for the system (Covas 1985). In this case, the opposite was observed and the more viscous PCL resides on the surface, suggesting that the affinity between the steel surface of the extruder die and PCL has a strong effect on the morphology. This effect may be enhanced by modifying the surface to favor one of the polymer phases.

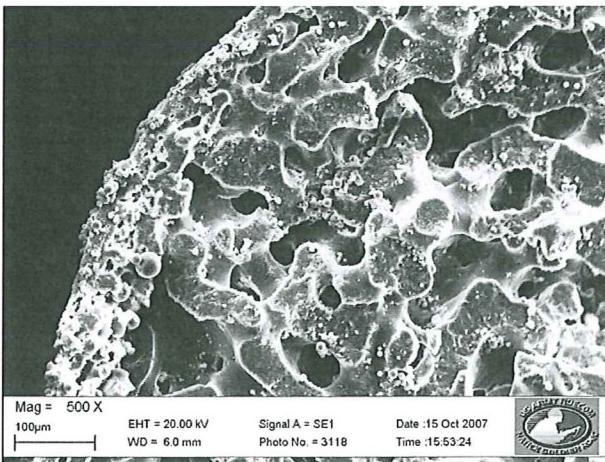


Figure 1a. Micrograph of PCL/PEO extrudate with PEO washed away, illustrating formation of skin-core morphology.

Figure 1b is a 2D Newtonian simulation of a 50/50 composition ratio with a boundary that favors one of the phases. It is clear there is an abrupt boundary between the skin and the co-continuous core. Figure 1c is the Power Law fluid case, $n=0.3^1$ (Middleman 1977). The same type of morphology is exhibited, with a core that is less disturbed by the flow field.

Figure 1d is a Newtonian flow at 65/35 composition with a strong wall attraction. The rapid segregation at the wall creates a double layer of A and B. In cases where the attraction is slower, only a single layer is produced. Note that the core is not co-continuous.

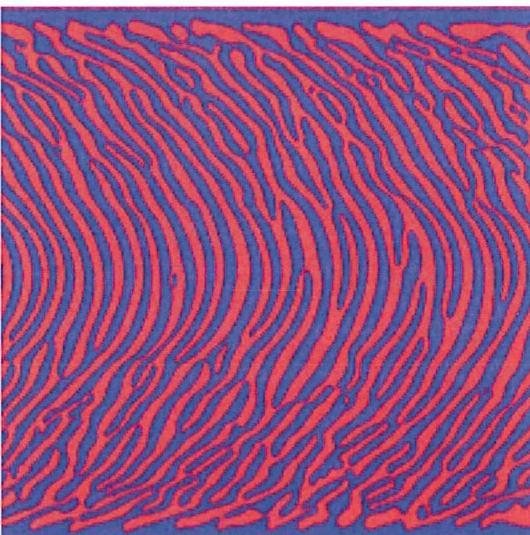


Figure 1b. Newtonian cell dynamic model of 50/50 blend of A and B, simulating skin-core morphology formation due to A wetting the surface of the exit die.

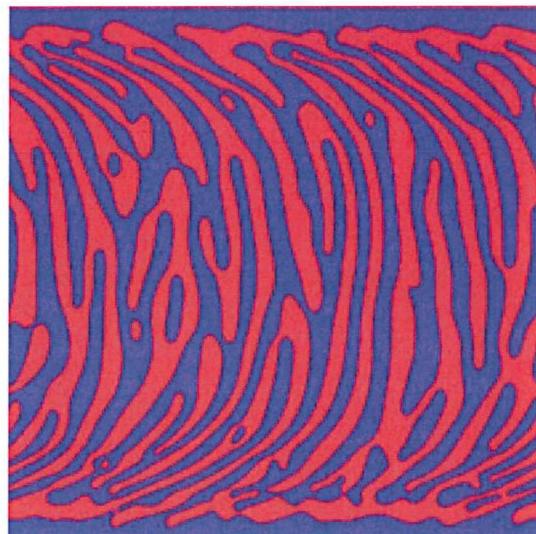


Figure 1c. In Power law fluid simulation, using same 50/50 composition and surface effect, the core is less disturbed by the flow field.

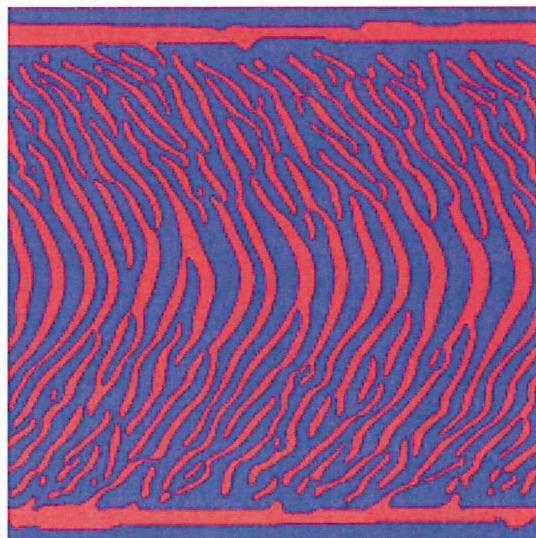


Figure 1d. Newtonian case of 65/35 blend of A and B and surface effect.

An interesting case is one in which there are two different surfaces. A simulation with “top” and “bottom” surfaces favoring A and B polymer phases results in a co-continuous core but with a skin of A on the top and a skin of B on the bottom with phase in contact with the co-continuous core, shown in Figure 2.

¹ The selection of this value is somewhat arbitrary. Dow Styron 666 a common polystyrene has $n = 1/3$ (Middleman 1977b)

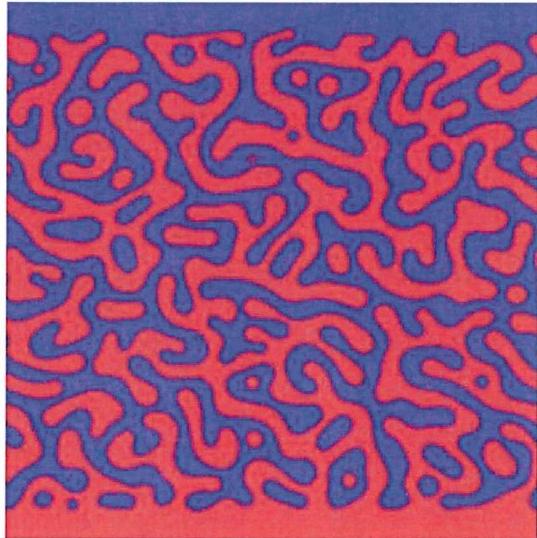


Figure 2. Simulation of 50/ 50 blend where component A wets the top surface and B the bottom surface. The core is a co-continuous morphology.

These results suggest that it should be possible in this system to create separate “contacts” on the surface by controlling the surface energy of the extruder die. Furthermore, we would like to be able to use control of the surface properties of the solid wall to create access to the interior features of the fiber. In a 3D cylindrical exit die it should be possible to create one or more stripes of B along the length of a fiber with the rest of the exterior comprised of polymer A. Possible applications are polymer heterojunctions for photovoltaic applications or other device fibers.

3.2 Effects of Flow Profile

At high flow rates polymers are typically shear thinning power law fluids. That presents both a challenge and an opportunity. Because the flow profile is different new features appear in the power law fluid. However, our laboratory extruder is running at much slower speeds and the polymers probably behave as Newtonian fluids.

Processed in the laboratory extruder the shear is distributed across most of the fiber cross section. In the power law case there is a high shear zone near the wall and a low shear zone in the center of the fiber. The development of high and low shear zones is enhanced by low values of n , which is a function of high molecular weight and high flow rates. The shape of the flow profiles for a Newtonian fluid and a power law fluid with $n = 0.2$ are clearly seen in Figure 3a and 3b, respectively. The high shear regions are where the velocity is changing most rapidly.

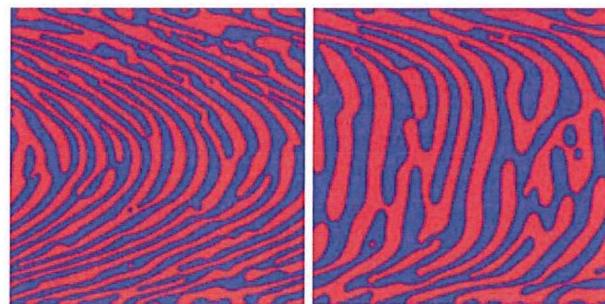


Figure 3a. Simulation of 50/ 50 blend of A and B with a Newtonian flow profile (left). 3b. Simulation of 50/50 blend of A and B with a power law fluid flow profile. Power law exponent, $n=0.2$ (right).

The presence of two distinct zones of shear will make the production of complex morphologies easier, since the interior of the fiber and the edge spontaneously form different morphologies. Elongated morphologies in the center of the fiber may be more difficult to achieve due to the lack of shear. In contrast, morphologies where the features are perpendicular to the flow direction will be easier to develop, illustrated in figure 3.

3.3 Fibril in Fiber Formation.

Experimentally (Drew 2007), for a 2:1 ratio of PEO to PCL, rods or fibers of PCL were formed within the larger extrudate. Even without any drawing the fibers were 1.7 microns in diameter. It should be possible to reverse the phases but due to viscous entrapment of the low viscosity PEO in water solution it was not observed. Figure 4 shows a typical fibril within fiber morphology.

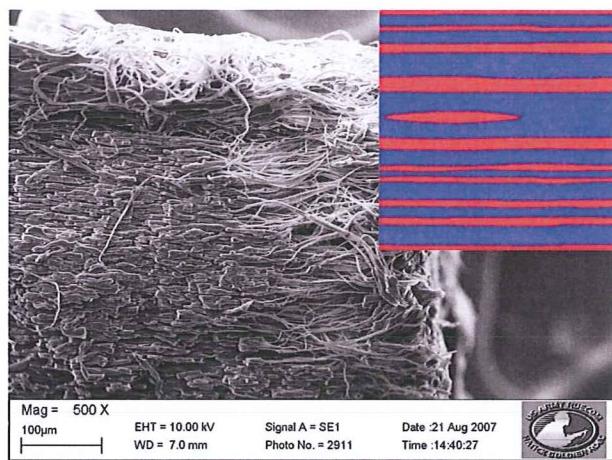


Figure 4. Fibrils formed within an extruded 2:1 blend of PEO:PCL with PEO washed out. Inset is a long time simulation of a 1.9:1 blend of A:B in pressure driven Newtonian flow.

The cell dynamics simulations of a 65/35 A/B composition (order parameter = 0.3, 1.9:1 ratio) in Newtonian flow over a long number of simulation time

steps, form fibers and rods of B within A. A snap shot of the simulation is shown as an inset in Figure 4. In this case the 2D simulation is ambiguous since the morphology could be lamellar.

Increasingly complex designs are possible, including more than two phase separating components combined with multicomponent spinning. To realize increasingly complex designs will require efficient modeling codes to investigate new structures before difficult and complex experiments are conducted.

CONCLUSIONS

Blending of immiscible polymers through phase separation is a commercially viable way to create nanostructured fibers. A multitude of novel materials can be created by this method including microfibrillar composites, composite biomaterials, electrically conducting blends, and nanostructured blends. The design and development of these multiphase materials depend primarily on interfacial control and morphology control. The ability to model the morphology development in the extrusion process with a simple 2D cell dynamics code will speed the development of these materials. Expanding this approach to include blends of polymer melts and polymer solutions presents an opportunity for the development of materials with increasing complexity. Nanostructured fibers offer the prospect for creating fiber devices that can be incorporated into composites and “smart” uniforms. Furthermore, by incorporating advanced materials into the composite such as biomaterials, ceramics and conducting polymers, biopolymer devices, power harvesting devices and sensor technology may be realized.

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REFERENCES

- Covas, J.A., et al., 1985: Rheological Fundamentals of Polymer Processing, in Coextrusion of Polymer Melts; Kluwer Academic: Boston, 1995. by Karagiannis A, Hrymak AN, Vlachopoulos J, Vlcek J. 265-288.
Drew, Christopher P., Bosseman, Suzanne E., and Ziegler, D., 2008: Mixed Morphology by Extrusion of Phase-Separated Blends of Melt Processed

Polymer and Polymer Solution, *J. Appl. Polymer Science*, in press.

Fan, J., Fedkiw, P.S., 1997: Composite electrolytes prepared from fumed silica, polyethylene oxide oligomers, and lithium salts. *Journal of the Electrochemical Society*, **144**, 399-408.

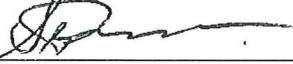
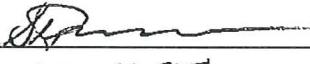
Middleman, S., 1977: *Fundamentals of Polymer Processing*, McGraw-Hill, 88, 147.

Oono, Y., and Puri, S., 1988: Study of phase-separation dynamics by use of cell dynamical systems. I. Modeling, *Physical Review A*, **38**, 434-453.

Park, Tae G., Cohen, S., Langer, Robert S., 1994: United States Patent #5330768.

Priya, Shashank, Islam, Rashed, Dong, Viehland, D., 2007: Recent advancements in magnetoelectric particulate and laminate composites, *Journal of Electroceramics*, **19**, 147-164.

Sims, C. Derek M.D.; Butler, Peter E. M. M.D.; Casanova, Rene M.D.; Lee, Betty T. M.D.; Randolph, Mark A. M.A.S.; Lee, W. P. Andrew M.D.; Vacanti, Charles A. M.D.; Yaremchuk, Michael J. M.D, 1996: Injectable Cartilage Using Polyethylene Oxide Polymer Substrates. *J. of the American Society of Plastic Surgeons: Plastic and Reconstructive Surgery*, **98**, 843-850.

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